DEVELOPMENT OF THE GC/MED SYSTEM AS A NON–GC/MS SCREENING TECHNIQUE FOR HAZARDOUS WASTES

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1. INTRODUCTION

This final report summarizes the work activities related to MOE Requisition No. 135226 on the Development of the GC/MED System as a Non-GC/MS Screening Technique for Hazardous Wastes. The analytical methodologies currently in practice for the identification and monitoring of hazardous waste using GC/MS are expensive, labour intensive and take a considerable amount of time for each analysis. This presents severe logistical problems associated with the identification and characterization of hazardous waste and hence there is a need to develop rapid screening methodology which could be adapted to large numbers of samples and reduce the need for GC/MS analysis.

Gas chromatography and microwave plasma emission detection present several opportunities for rapid screening since the technique determines the specific element abundance (i.e. fluorine, chlorine, bromine, phosphorous, carbon, and sulphur) for each compound and hence reduces the need for high resolution gas chromatography for identification. This unsolicited program was a three phase program comprising: Phase I - Instrumentation Development and Optimization; Phase II - Analytical Methodology for Rapid Screening; and Phase III - Developing and Testing of Analytical Protocol.

Although the work in Phase I was completed and the analytical methodology in Phase II developed, the technique could not be successfully implemented due to difficulties encountered with the detection of PCB's.

The report described herein discusses the work accomplished and the problems encountered with the detection of PCB's as proposed in this contract, and discusses future work follow-up.

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2. PRINCIPLE OF OPERATION

The Helium Microwave Plasma (MIP) Emission Detector is based upon the measurement of emissions produced by the interaction of microwave frequency electromagnetic fields with gases eluted from a gas chromatograph.

The capillary column of the gas chromatograph is fed through a heated transfer line into the plasma torch and positioned within a few millimetres of the plasma discharge. The plasma support gas, introduced through the 'T' junction, is preheated in the GC oven prior to its entrance into the transfer line. The support gas merges with the GC eluent in the MIP torch just a few millimetres from the plasma.

A compound introduced into the plasma is partially dissociated resulting in molecular fragment and atoms in an electronically excited state. The resultant optical emission radiation is focused onto an entrance slit of a multichannel spectrometer. The degree of molecular fragmentation and optical excitation is a function of the microwave induced power input and the compound stability. Simple halocarbons very easily lose their first halogen atom with a relatively high efficiency. However, others like PCB's, are very stable and the degree of dissociation of chlorine from a PCB molecule is very inefficient by microwave plasma alone. Quantitative evaluation of overlapping singly and polychlorinated compounds poses additional difficulties since the quantity of each compound is derived from the compounded intensity of the radiated light, the number of excited atoms originating from multi-chlorinated molecules will be higher than from single chlorinated molecules. In high resolution chromatography GC/MED can easily be calibrated, however, in the present case when many compounds coelute together, quantitative calibration becomes much more difficult.

2.1 DETAILED SYSTEM DESCRIPTION

2.1.1 General

The helium microwave plasma emission detector consists of a multichannel spectrometer, microwave cavity assembly, GC interface, gas supply unit, and microwave power generator. Figure 1 shows a block diagram of the helium microwave plasma emission detector.

2.1.2 Spectrometer

Initially, the spectrometer selected for the studies was a direct reading spectrometer manufactured by Applied Research Laboratories, Model QA-137. The original diffraction grating was replaced with a new one in order to cover the span of analytical wavelengths for selected elements. The system required optical alignment to accommodate the new diffraction grating and the new positions for the secondary slits for the elements selected. Unfortunately, the light collecting efficiency of this instrument was too low and the system was replaced with a more compact one designed by Barringer Research.

The Barringer multi-channel spectrometer (MED 650) provides a multi-element detection of the emitted light. The light, emitted from the plasma, is focused onto the primary entrance slits by a single quartz conductor lens in an adjustable holder. The elements selected for the analysis and their respective wavelengths are shown in Table 1. As is seen in Table 1, most of the radiation measured is in the narrow visible band region, therefore, the use of a lense rather than mirrors is satisfactory. The radiation from the carbon and phosphorous, however, could not be focused properly when image focusing is performed in the visible region. Emission from
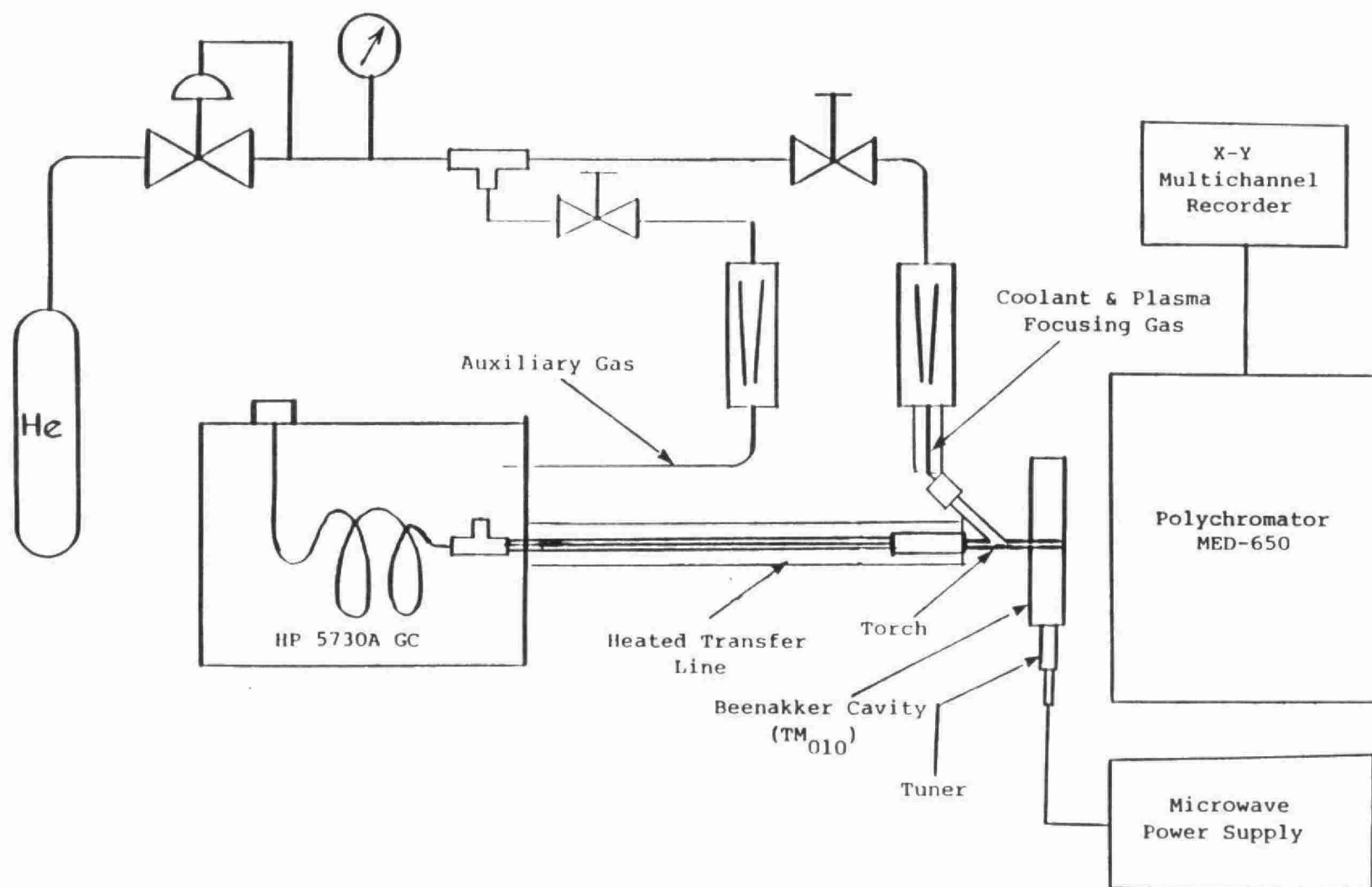
Figure 1   Schematic Diagram of the Experimental Set-up with Codding Torch

TABLE 1

Analytical and Background Correction
Wavelengths in the MED 650

Element	Analytical Wavelength, (nm)	Background Wavelength, (nm)
C (2nd order)	193.09	194.07
P (2nd order)	213.62	214.61
Br (1st order)	470.48	471.48
Cl (1st order)	479.45	480.45
S (1st order)	545.39	546.39
F (1st order)	685.60	686.57

carbon is very strong and thus no problem is encountered with this element. Detection of phosphorous, however, would be limited and use of optical mirrors would be more appropriate should low detection of phosphorous be of importance. The use of mirrors is more cumbersome and the system cannot be made as compact as with lenses.

The optical layout of the multichannel spectrometer is shown in Figure 2. The entrance slits, concave diffraction grating and all the exit slits are located on the Rowland circle. The light from the exit slit is reflected by a plane mirror to the photomultiplier.

The 500 mm spherical radius reflection grating has 1180 lines/mm and dimensions of 50 x 30 mm^2. The first order reciprocal dispersion is approximately 1.6 nm/mm. The diffraction order sorting filters, positioned in front of the photomultiplier tube holders, were used to separate first diffraction order from the higher ones.

In order to enhance background rejection, modulation is implemented by means of alternately exposing two entrance slits of the spectrometer with a chopper disc. Each channel can be corrected at approximately 0.9 nm on either side of the analytical wavelength, so that the photomultiplier behind each exit slit sees, alternately, background and background plus signal. The electronic subtraction of the 'ON LINE' and 'OFF LINE' signals can significantly reduce the contribution of background and its fluctuations. However, one must be aware that the background slit (0.1 mm wide x 3 mm high) is displaced in space by 0.6 mm from the signal entrance slit. For a non-uniform or point source background, as is seen on the background slit, may be quite different from the background
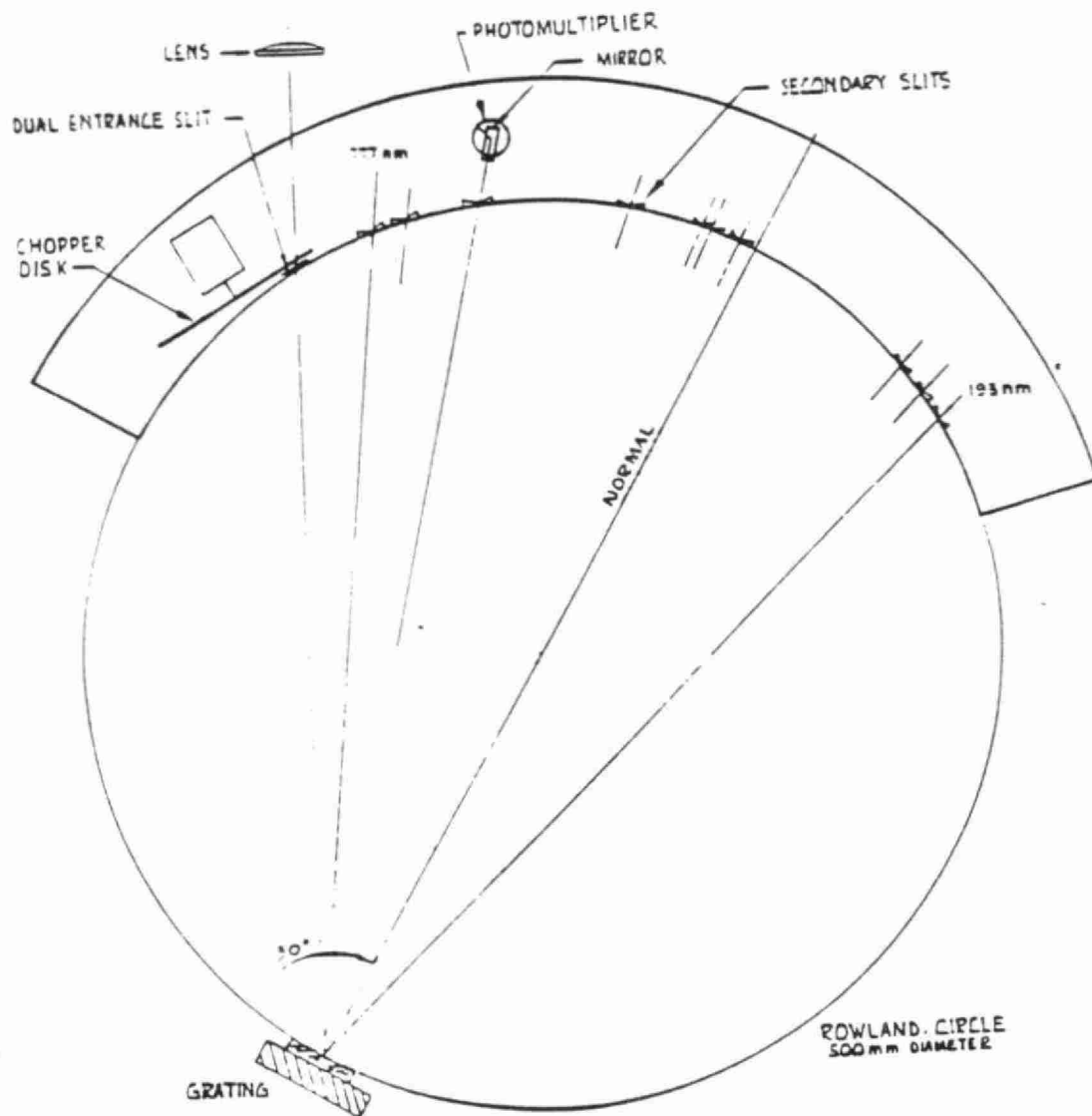
Figure 2   Optical Layout of Multichannel MED 650 Spectrometer

radiation as it appears on the signal slit. If the source is
stable (in space) with proper focusing of the source onto the
two slits, the major background signal from the molecular
emission bands are minimized.

2.1.3 Microwave Plasma Source

The microwave induced plasma operates at a frequency of 2450
MHz and is used as an excitation source for optical emission
spectroscopy analysis. The plasma is formed in a quartz
discharge tube placed in a cylindrical cavity to which power is
applied from a microwave generator via a coaxial transmission
line.

The stray microwave radiation has been measured at all points
around the cavity, transmission line, tuner and the generator.
Maximum detected value did not exceed 0.02 mw/cm^2 at 5 cm.

2.1.3.1 Cavity and Impedance Matching

The present cavity is based on the original design by C.I.M.
Beenakker (6) and consists of a cylinder with a fixed bottom
and removable top. The cavity has an internal diameter of 92.7
mm and height 10 mm and is made of copper. All the internal
surfaces are polished and silver plated for improving quality
factor and finally flashed with gold for protection. The
removable lid is firmly attached to the cylindrical cavity by
twelve equally spaced screws, to ensure good electrical
contact. The plasma discharge tube is mounted in the center of
the cavity. The microwave coupling loop is extended into the
cavity and one end is attached to the cavity wall and the other
to the Amphenol UG-58 connector.

Holes in the cylindrical wall of the cavity are made for air cooling and for viewing. The cavity is attached to the bracket positioned on a bi-directional adjustable stand.

Impedance matching is accomplished by a double slug tuner (mod. SF-31N, Microlab/FXR) positioned between the cavity and the coaxial transmission line.

2.1.4 Microwave Generator

A microwave generator (EMS, Microtron 200 Mark III) supplies output power continuously variable between 0 and 200 W. The generator is equipped with a total power output meter and reflected power meter. The difference in reading from these meters is not a measure of power directly applied to the plasma, since a large amount is dissipated as heat in the cavity.

2.1.5 System Gas Flow

The gas flow diagram is shown in Figure 2. Carrier gas helium from a main supply is regulated to about 30 psig. A heated and insulated transfer line is connected on one side to the gas chromatograph through a "T" to a capillary column and the plasma support gas. The support gas is preheated in the oven before entering the transfer line around the capillary column. The capillary column is threaded through the transfer line and directly into the torch, at which point the make-up gas picks-up the GC eluent and carries it into the plasma region. The 'Coolant and Plasma Focusing Gas' as indicated in Figure 1, is used only with the Codding torch.

2.1.6 Microwave Discharge Torches

Three types of microwave discharge torches were investigated in this study: two capillary torches and a Codding torch (8). One capillary torch was made from a quartz tubing of 6 mm OD and 0.8 to 1.0 mm ID. The second capillary torch was made from alumina with 6 mm OD and 0.8 mm ID. The third type of torch used was the Codding torch (8), a schematic diagram of which is shown in Figure 3. It is made from two concentric quartz tubes arranged similar to a conventional ICP torch. The threaded quartz insert (4 mm OD, 0.8 mm ID) generates a tangential gas flow which focuses the plasma and keeps it away from the wall and thus prevents the torch from being eroded at high power inputs. The thread is cut into the insert at a pitch of 10 and two threads of 0.5 mm wide and 0.6 mm deep are interspaced to yield a linear spacing between them of 1.27 mm.

2.1.7 Gas Chromatograph

The HP 5730A gas chromatograph was equipped with an EC detector and 15 m J and W fused silica megabore column (DB-17, 1 um film).
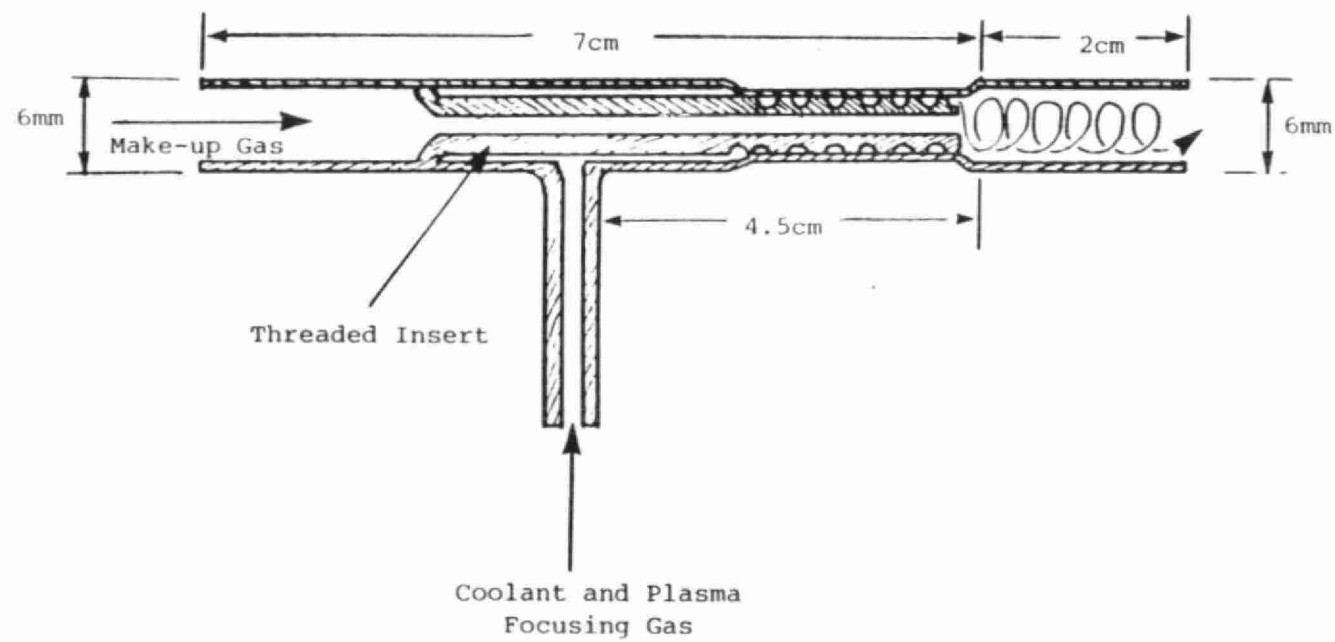
Figure 3   Schematic diagram of the Codding Plasma Discharge Torch

3. RESULTS AND DISCUSSION

The initial study was conducted with a capillary torch and a
modified ARL (model QA-137) high resolution monochromator.
Being a high resolution instrument sensitivity was rather low
(light collecting solid angle small) and hence a spectrometer
designed and built for Environment Canada by Barringer Research
(MED-650) was used for subsequent studies. The sensitivity and
selectivity for the capillary torch and MED-650 spectrometer
for simple halogenated hydrocarbons was observed to be good as
is seen in Table 2. Table 2 also summarizes the selectivity of
the GC/MED system with respect to carbon. Figure 4 is a GC/MED
multi-channel record of a number of organic compounds
containing F, Cl, Br and P. Initial studies on the detection
of chlorine have indicated a strong correlation between power
and signal intensity. An example of this is displayed in
Figure 5 for chlorine and carbon signals as breakdown products
of chlorobenzene.

The capillary torch plasma was found to be stable only at low
loading (about 0.025 uL) and low power. In order to prevent
the plasma from extinguishing during the solvent elution, it
was necessary to employ GC in the split mode (1:40 for a 1 uL
injection sample). Thus, with pg/s sensitivity the actual
concentration of the analyte in the sample for detection is in
the nanogram per uL concentration range. In addition to
problems associated with loading, the breakdown efficiency for
more stable halogenated hydrocarbons such as PCB's was observed
to be very low. Traces of the PCB breakdown were observed by
increasing the power to 120 watts. However, at powers
exceeding 85 watts the life time of the torch was considerably
reduced and at 120 watts the torch lasted for only a few
minutes.

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TABLE 2

Detection Limits and Selectivities
for Simultaneous Determination [1]
with Capillary Torch

Element	Compound	Detection[2] Limit, pg/s	Selectivity vs. C[3] Using n-decane for Carbon Signal
Br	$CHBr_3$	27	180
C	$C_{10}H_{22}$	4	1
Cl	C_6H_5Cl	12	200
F	$C_6H_4CH_3F$	11	366

(1) Plasma operating conditions 85 watts incident power, 0-2
   watts reflected power, 50 mL/min He plasma support flow
   rate.

(2) Detection Limits $= \dfrac{W_{analyte} (pg)}{w_{1/2}(s)} \cdot 2 \dfrac{h_{noise}}{h_{signal}} \dfrac{pg}{s}$
   (Signal/Noise=2/1)
   where $w_{1/2}$ line width at half maximum in seconds
   and W is the weight of analyte being monitored, e.g. Cl.

(3) Selectivity = (h/W)analyte/(h/W) carbon contribution on
   analyte from n-decane. It is assumed that half widths are
   the same. If different, correction as in (2) above must be
   incorporated.

F-channel
$C_6H_4CH_3F$

Cl-channel
C_6H_5Cl

Br-channel
$CHBr_3$

P-channel
$(CH_3CH_2)_3P$

C-channel

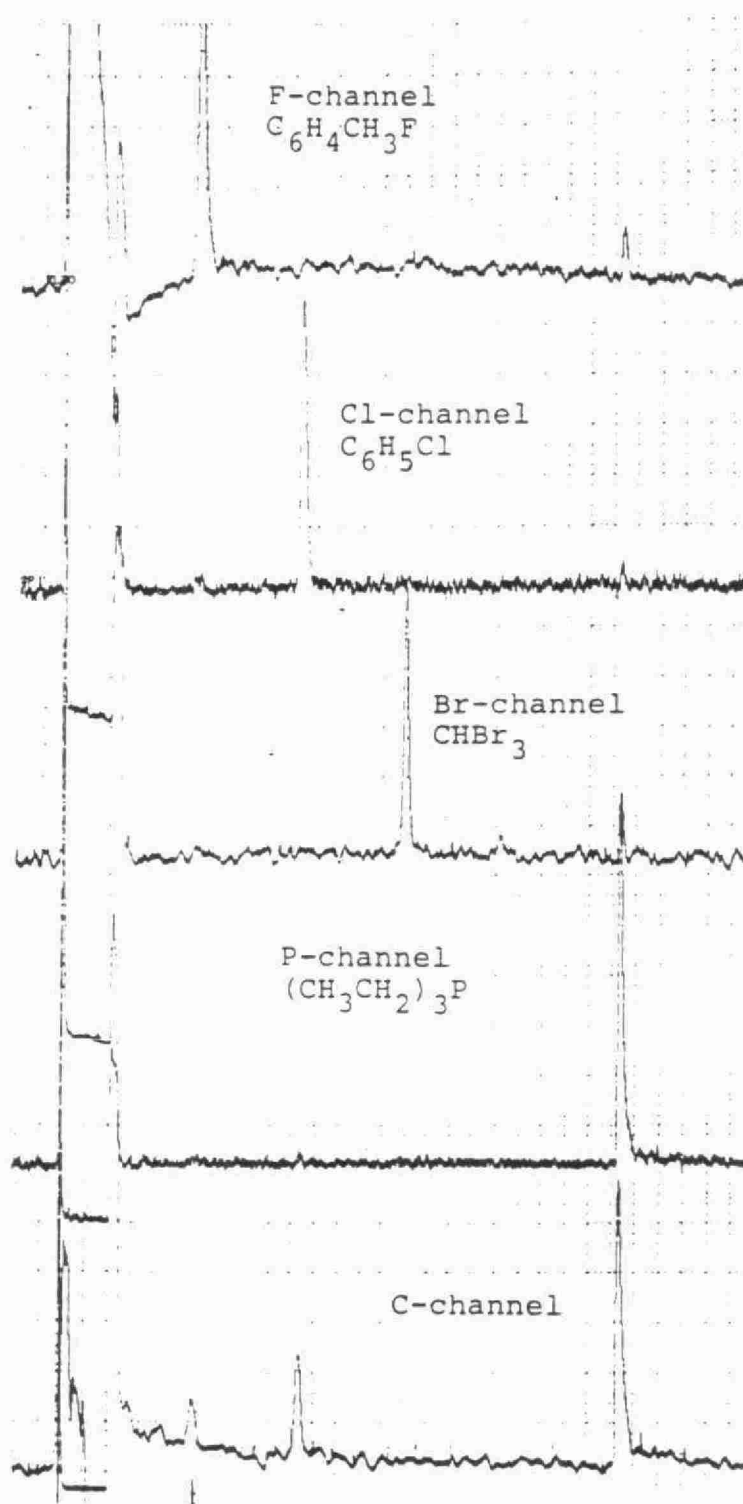Figure 4   GC/MED Multichannel Record
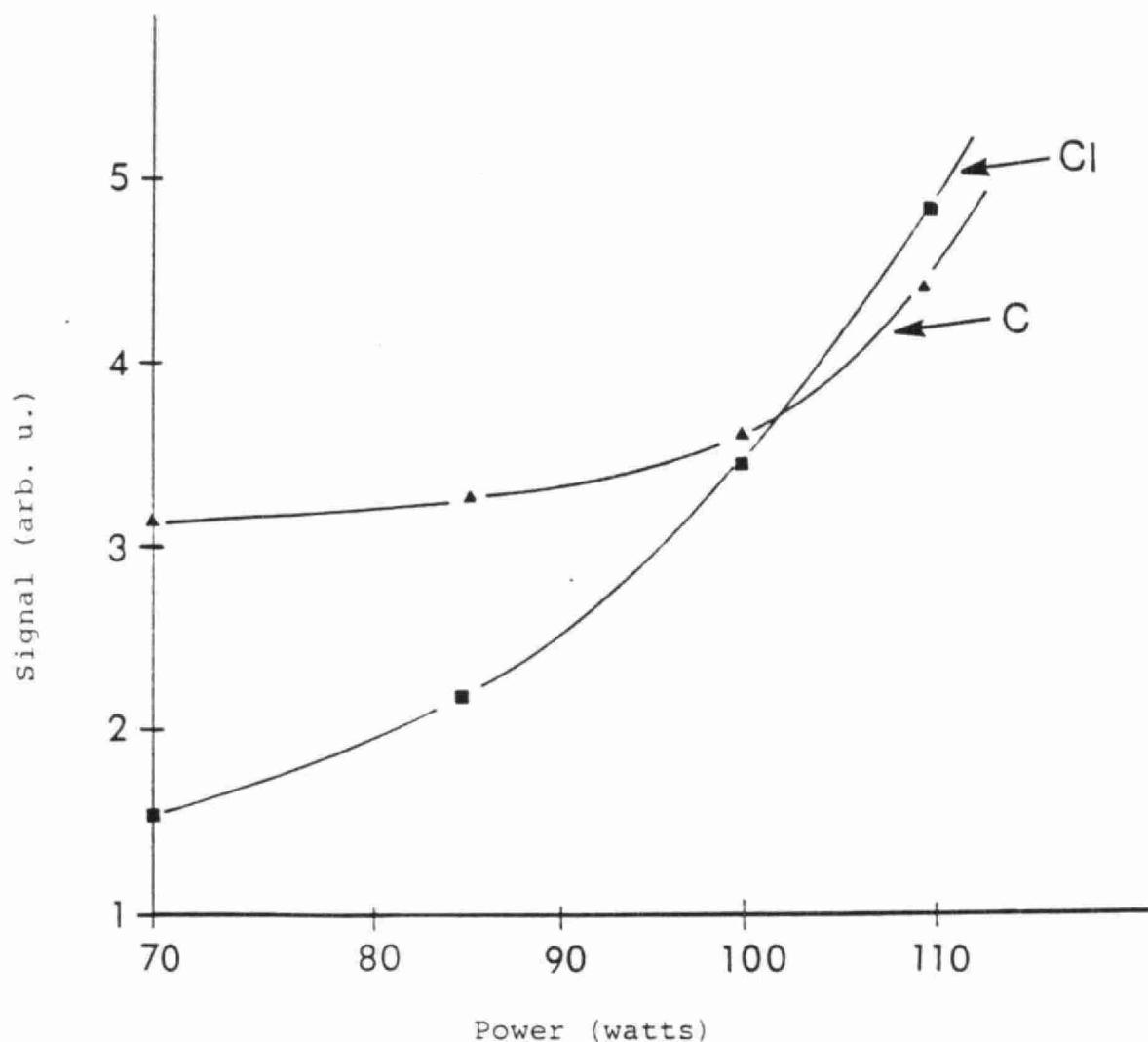
Figure 5   Chlorine and carbon signal from chlorobenzene as a
            function of incident power using capillary torch and
            MED 650 polychromator.   GC conditions: Isothermal run
            at 100°C, with split ratio of 1:40, 1 ul injection
            volume of 60 ng/ul of Cl on 15 m megabore DB-17 column.

The characteristics of the capillary torch requiring low sample loading and operating power presents severe limitations with respect to the application of rapid screening of halogenated compounds. Hence, a microwave torch designed by Codding (8) was evaluated for high power operation. Figure 3 is a schematic diagram of the Codding torch. Gas introduced along the spiral of the inner tube acts as a coolant and plasma focusing gas. The GC column is terminated just before the end of the threaded inner tube and the torch is inserted into the Beenakker cavity with the threaded end just before the cavity. In order to keep the plasma stable and focused, and to attain a quick plasma recovery after the solvent front, the coolant gas flow was maintained at about 500 cc/min with the auxiliary and carrier gas set to 50 to 80 cc/min. Both auxiliary and coolant gases were preheated in order to prevent analyte condensation. The schematic diagram of the experimental set-up is shown in Figure 1.

The Codding torch was observed to reduce the sensitivity of the MED by more than two orders of magnitude compared to the capillary torch for simple halogenated hydrocarbons. The reduction in sensitivity with the Codding torch is believed to be primarily due to a sample dilution, spatial distribution and residence time reduction of analyte in the plasma region. However, this reduction in sensitivity was largely offset by the capability of accepting a much larger loading into the Codding torch without extinguishing the plasma. The plasma could be sustained with sample loadings up to 10 uL, however, the signal strength as a function of sample volume was non-linear and past the first two microliters the gain in signal strength decreased very rapidly.

The Codding torch could be operated continuously at 170 watts without any noticeable deterioration to the torch. At a power

input of 180 to 190 watts, PCB's in the high nanogram range could be detected. The GC/ECD and GC/MED chromatograms of Aroclor 1260 are shown in Figure 6. The good correspondence between the GC/ECD and GC/MED chlorine peaks indicate that the PCB's are being broken down in the helium plasma. However, the very low signal and the decrease in the chlorine and carbon signal for the higher chlorinated PCB's indicate that the breakdown is very inefficient even at 190 watt incident power.

Serious problems were also encountered with the lack of signal reproducibility using the Codding torch. It was not uncommon to find a temporary loss of signal for the chlorine channel and then recovery of the signal on the subsequent run. The lack of signal reproducibility with the Codding torch greatly hampered system optimization. It is believed that the lack of signal reproducibility is a result of the plasma's shifting position after solvent elution. The MED spectrometer operates with on-line/off-line background correction using a chopper disk with dual entrance slits. The signal from one slit represents the signal plus background and the other slit is the background alone. Since background correction is performed in real time, errors could result if the plasma wanders in and out of the two slits.

From studies with the capillary and Codding torches, it became clear that PCB's cannot be broken down by the plasma alone and as has been suggested by Dr. D. Boomer, the GC eluents were heated up to 760°C prior to the entrance to the helium plasma. For that purpose, the quartz capillary torch was connected to the 6 mm OD alumina tube through zero volume union. The capillary column was extended just in the alumina tube. The alumina tube was maintained at 760°C while the transfer line was kept at 250°C. Power input to the MIP was maintained at 90 watts. The inside diameter and distance from
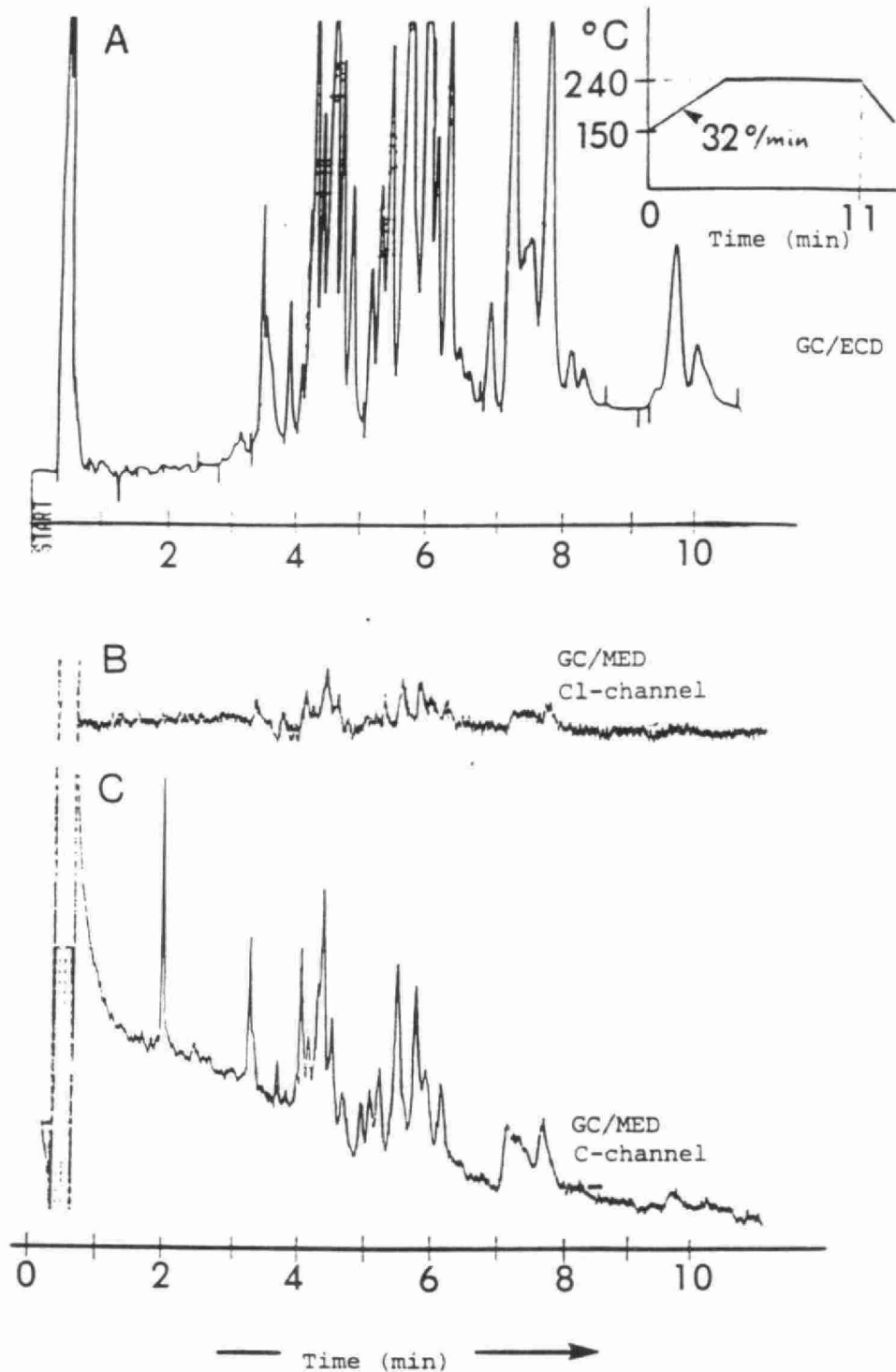
Figure 6   Chromatogram for Aroclor 1260
            A - GC/ECD run with temperature programming as indicated;
            B - GC/MIP run on chlorine channel;
            C - Simultaneous GC/MIP run on carbon channel at incident
                microwave power of 190 watts and reflected power of
                5 watts.

the elution point to the plasma were kept to a minimum to sustain chromatographic integrity as much as possible. The resulting chromatogram of PCB's is shown in Figure 7. The degree of break-down of PCB's with preheating is at least an order of magnitude higher than without preheating. The higher chlorinated PCB's not detected on GC/MED without preheating were now observed. Unfortunately, the heat transferred from the heated section to the capillary torch, in addition to dissipated power from the microwave plasma, caused a very rapid deterioration of the torch at an operating power of 75 watts. Somewhat slower, but similar deterioration was observed with the Codding torch operated at 90 watts MIP power. The alumina torches were being destroyed by cracking around the circumferance at the centre of the maximum plasma intensity, i.e. at the middle of the microwave cavity.

To avoid the destruction of the torches, the thermal cracking of the GC eluents should be moved away from the torch. To preserve the chromatographic integrity a short section of an uncoated megabore column could be used to deliver the products into the torch. The two extreme ends of the heated alumina tubing must be cool enough to prevent the capillary columns from melting.
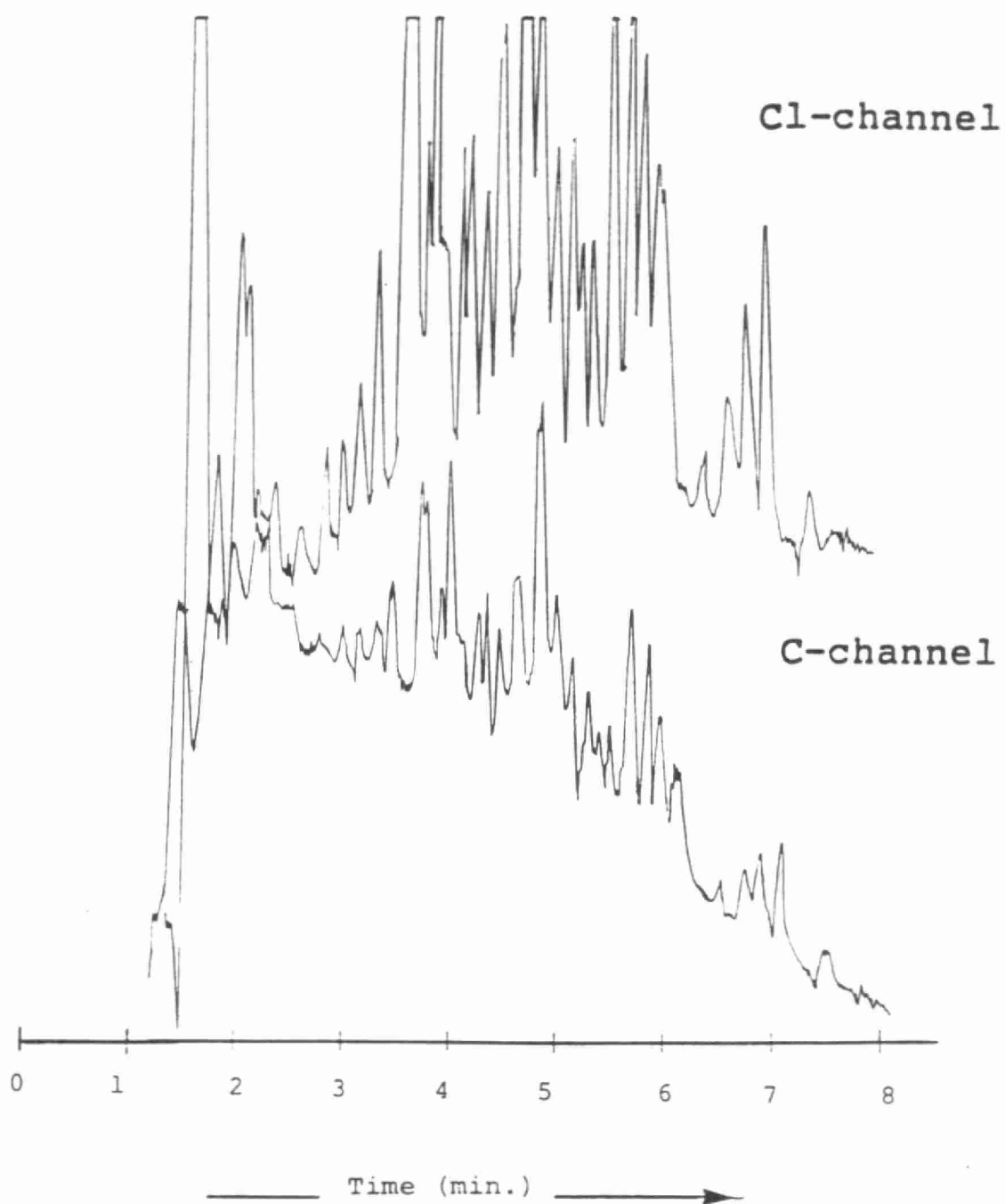
Cl-channel

C-channel

Time (min.)

Figure 7   GC/MED Chromatogram of Aroclor 1260 with the GC Eluent
          Preheated to 760°C before entering the plasma.

4. CONCLUSIONS

The necessity of monitoring halogenated compounds cannot be over emphasized, because many are known to be carcinogenic or toxic. More than half (72) of the non-metallic priority pollutants (114) fall into the halocarbon category. With these increased demands on sample throughput the development of techniques for a rapid total organic halogen determination is very important.

GC/ECD is at present the most sensitive technique for halocarbon determination, however, ECD is prone to contamination and overloading and thus extensive sample clean-up is necessary.

The advantages of the MED over many other detectors are as follows:

1. Linearity over a wide dynamic range (two to five orders of magnitude);

2. Low detection limits, in ppb levels, for many simple halogenated hydrocarbons;

3. Multi-element detection which in turn requires low resolution; and

4. High loading capacity and fast clean-up if overloaded.

Extending these useful features into practical application, the MED could be used for the determination of pesticides, thermal insulators, plasticizers, and, by implementing some external means of partial atomization prior to the microwave excitation, PCB's.

By combining GC with MED partial spatial separation can be attained over a short period of time. Utilizing a simultaneous multi-element analysis remains a strong asset of the system.

However, further investigation is required to permit the plasma operation at higher power levels without destruction of the plasma torches is necessary. Thermal cracking of analytes such as PCB's should also be further investigated. Automated impedance matching is another area where more fundamental investigation is needed for routine analyses applications. These studies are more fundamental in nature and are beyond the current scope of the program.

The capillary torch has several advantages over the Codding torch, namely, low gas consumption, low cost, ease of operation and plasma focusing with excellent spatial stability. However, some serious disadvantages such as low solvent loading capacity and low operating power resulting in the inability of the plasma to breakdown the more stable compounds (i.e. PCB's) limit its usefulness in the arrangement investigated in the present study.

The Codding torch has several advantages over the capillary, but its disadvantages seem to neutralize its advantages. The plasma centering in the Codding torch occurs because of the gas pressure in the centre of the tube is less than at the outer edges. This provides a greater mean free path for the charged particles interacting with the electric field at the centre of the tube, resulting in reduction in tube degradation, ability to operate at higher MIP power, and large solvent loading capacity. However, increased gas flow (to centre the plasma, 300 to 700 cc/min) reduces available residence time in the plasma resulting in reduced sensitivity. Difficulties in focusing the plasma and possible shift in plasma after solvent

elution makes it difficult to optically couple the plasma image to the spectrometer. Also difficulties in manufacturing identical torches as well as the high cost of manufacturing these torches makes the use of these torches rather unappealing.

5. RECOMMENDATIONS

The application of the GC/MED to the rapid screening of
hazardous wastes requires further fundamental investigation of
the torches, cavities and optical coupling of the emitted
radiation to the spectrometer. Also, implementation of a
partial atomization prior to the microwave excitation of the
target compound appears to be necessary for the detection of
stable halocarbons and hence is worthy of further investigation.

The system does not have the capability of identifying specific
compounds and is capable of quantifying the target elements.
For qualitative and quantitative identification of compounds, a
library of target compounds with their retention times and
sensitivities would have to be established. The breakdown
efficiency will be a function of both type of compound, the
input microwave power, and the degree of analyte breakdown
prior to its excitation in the plasma. A library composed of
various suspected pollutants would have to be accumulated and
computer software developed to facilitate in identifying both
qualitatively and quantitatively the target compounds. For a
fast screening application on complex mixtures, only
semi-quantitative and qualitative identification can be
expected. A modified method of bringing emission light into
the monochromator entrance slits, like fibre optics, should
also aid in better source focusing. Implementation of the
solvent venting technique may also greatly improve the plasma
stability and should be considered in further studies.

Many of the problems identified in the development of the
GC/MED system for hazardous waste require research of a more
fundamental nature rather than instrument and analytical
methods development. This type of research is best carried out
in academic institutions rather than industry.

Dr. Eric Salin, McGill University, has expressed interest in conducting follow-on studies of the GC/MED. Despite the problems encountered in this study, Barringer remains optimistic in the technology. As part of our commitment, Barringer has agreed to lend the appropriate instrumentation and provide technical support for the follow-on studies if the proposal submitted to MOE was favourably reviewed.

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